Low Temperature Flux Growth of 2H-SiC and β-Gallium Oxide

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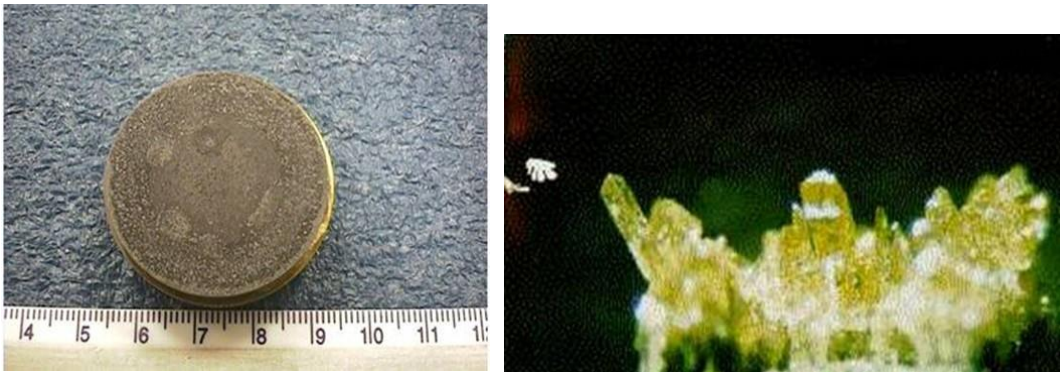
ABSTRACT

We present brief overview of our study on the low temperature flux growth of two very important novel wide bandgap materials 2H-SiC and β-gallium oxide (β–Ga_2O_3). We have synthesized and grown 5mm to 1cm size single crystals of β-gallium oxide (β–Ga_2O_3). We used a flux and semi wet method to grow transparent good quality crystals. In the semi-wet method Ga_2O_3 was synthesized with starting gallium nitrate solution and urea as a nucleation agent. In the flux method we used tin and other metallic flux. This crystal was placed in an alumina crucible and temperature was raised above 1050 ºC. After a time period of thirty hours, we observed prismatic and needle shaped crystals of gallium oxide. Scanning electron microscopic studies showed step growth morphology. Crystal was polished to measure the properties. Bandgap was measured 4.7eV using the optical absorption curve. Another wide bandgap hexagonal 2H-SiC was grown by using Si-Al eutectic flux in the graphite crucible. We used slight AlN also as the impurity in the flux. The temperature was raised up to 1050C and slowly cooled to 850C. Preliminary characterization results of this material are also reported.

INTRODUCTION

Since past several decades researchers are investigating substrates and devices for high power and low noise microwave devices for improving commercial and military systems. Great demands for the efficient, broad-band power RF transmitters with high linearity, as well as low noise rugged receivers for T/R modules cannot be achieved without great improvements in wide bandgap materials. Inspite of tremendous progress in GaN development and film technology defective nitride film technologies can only be looked upon as a 'stop gap' until high quality reliable defect-free structures are obtained. The poor quality of GaN film is the biggest problem in transitioning these practical devices to large production. There are many reasons for this show stopper. The unavailability of lattice-matched and chemically-matched substrate for GaN is perhaps the most important factor. The substrate choices which have been considered are MgO, Si, SiC, GaAs, AlN, GaN and ZnO. Several experiments [1-5] have been performed to grow pure and doped AlN large diameter crystals. Edgar and his coworkers [1-2] and group at Northrop Grumman have studied pure and SiC-AlN alloys to achieve cm size AlN crystals. Due to very high temperature involved and reactivity of Al with crucible materials, it was observed that growth of large crystals always had incorporation of impurities in the AlN bulk materials (**Figure 1a**). Some of our experiments using pure aluminum and nitrogen [5, 6] resulted in transparent large colorless hexagonal and needles with long aspect ratio (**Figure 1b)**. It was very difficult to control seeded growth due to several factors including low vapor pressure of AlN. During the growth long size needles, we observed growth of hexagonal small crystallites (**Figure 2**). For the growth of large crystals, when temperature was above 2150C the AlN single crystal changed to a yellow color due to impurities. All these problems indicate that very high quality large transparent materials of this composition could not be achieved by physical vapor transport. On the other hand large 4H-SiC and 6H-SiC have been grown in different sizes and are widely used for the hexagonal GaN thin and thick films with some surface modification. Since very recently it has been thought that 2H-SiC which has largest bandgap and mobility compared to other polytypes of SiC is not stable. However recent work in Japan flux using Lithium and nucleation with AlN has demonstrated that 2H-SiC growth is possible as a hexagonal substrate. Another exciting and new material gallium oxide, β-Ga_2O_3 is hexagonal and crystals have better chemical computability and favorable properties as a substrate for epitaxial growth of gallium nitride (GaN). The details of available commercial substrates such as AlN, SiC and Al_2O_3 along with β-Ga_2O_3 are given in Table 1. We will summarize the nucleation and morphology of 2H-SiC and describe the recent development in growth of β-Ga_2O_3 crystals.



(a) **(b)**

Figure 1- (a) AlN bulk fabricated and (b) cm size needle crystal grown using Physical vapor transport method.

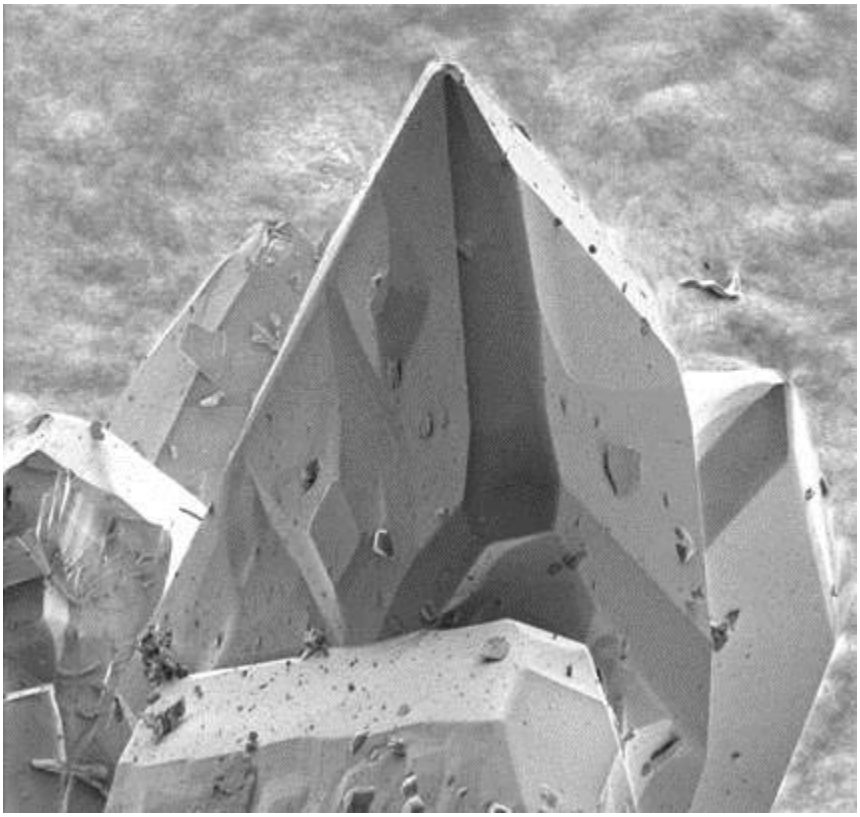


Figure 2- Growth of hexagonal small crystallites on the surface of large crystallites

As shown in Table 1, the bandgap of b- Ga_2O_3 is 4.9 eV, which corresponds to the second largest bandgap after that of diamond among semiconductors. The preliminary reported thermal conductivity and mobility are comparable to SiC and GaN. This combination of properties will enable to develop β- Ga_2O_3 deep ultraviolet photo detectors and high power amplifiers for variety of commercial applications in daily life. We will present preliminary results on a novel wide bandgap material β-Ga_2O_3 which also has much favorable properties for low temperature growth and fabrication.

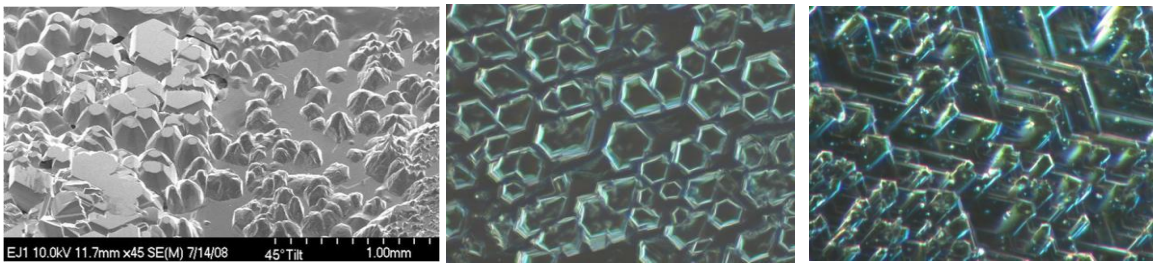
Table 1. Properties of commercial substrates are compared with β-Ga_2O_3

Figure of merit for carious semiconductor materials

	Si	4H-SiC	GaN	Diamond	β-Ga_2O_3
Bandgap (eV)	1.1	3.18	3.3	5.5	**4.85**
Electron Mobility (cm^2/Vs.)	1400	700	1200	2000	**400**
Breakdown Field E_b (MV/cm)	0.3	2.5	3.3	10	**8**
Dielectric Constant	11.8	9.7	9.0	5.5	**9.5**
Baliga's Figure of Merit	1	340	870	24664	**3444**

2. EXPERIMENTAL METHOD AND RESULTS

2.1 Growth of 2H-SiC Material: In the past many years we have used the physical vapor transport method in a manner similar to that used for silicon carbide and aluminum nitride described in references 3-5. All the growth experiments were performed in a vertical transport geometry in which the source material was transported upward into a cooler zone. In this investigation we used a combination of Czochralski and flux growth method. A graphite crucible was used as container and Al-Si eutectic was used as nutrient and flux. We used a typical flux of 100 gm and mixed by melting. Eutectic completely melted above 660C. However, we raised the temperature to 1050C and added 1-2 gm AlN powder. The stirring was performed using a ceramic rod with very thin tip containing SiC substrate. The silicon reacted with graphite and when we cooled the crucible, small crystals grew on the SiC substrate. In the beginning SiC substrate dissolved quickly. Several test runs were performed to avoid dissolution and Si concentration was maintained to keep near eutectic.



(a) (b) (c)

Figure 3- Morphology of (a) nucleation (b) small crystallites and thick film of SiC

The normally-unstable 2H-SiC crystal type appear to be stabilized by AlN deposits. In the presence of AlN the SiC nucleates and deposits begin as discs, growing to become pyramids, before finally coalescing to become a continuous layer. 2H is the natural crystal orientation of AlN. The SiC deposits begin as discs and grow to become pyramids, which forms small crystals before finally coalescing to become a continuous layer. There is a continuous growth and etching on the substrate surface. This type of behavior was observed by Edger as well as Swedish researchers also. Presence of AlN forces nucleation as the hexagonal. Some very old researches based on SiC-AlN composites have indicated that hexagonal morphology was always observed even in small concentration range of AlN. Further analysis by transmission electron microscope (TEM) is required to resolve this issue. However previous TEM studies by Wagner, Singh and Berghmans shown in **Figure 4** shows evidence of 2H-SiC on 6H-SiC substrate.

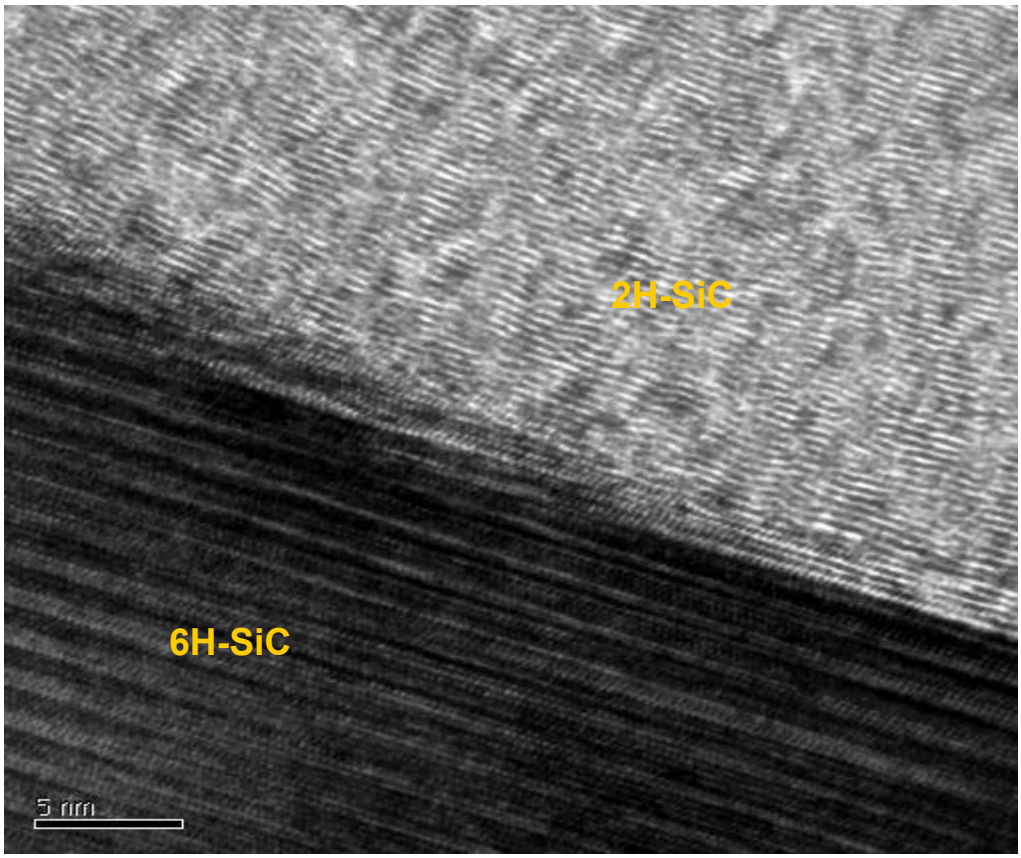


Figure 4- TEM of grown 2H-SiC on 6H-SiC substrate (Unpublished results of B. Wagner, A. Berghmans, D. Knuteson and N.B.Singh)

2.2 Growth of β-Ga_2O_3 crystals: In past five years crystal growth of β-Ga_2O_3 has become very interesting subject. The problem lies in the nature of the phase-diagram of this material. A very flat congruent compound has been reported at the 60atomic % of the oxygen in the Ga-O phase diagram above 2300C. This requires control of oxygen pressure, a stable crucible and control of volatile impurities. Because of these problems we adapted low temperature flux growth method. In both cases w used semi-wet methods for this material. Crystal growth studies to demonstrate 2H-SiC [7-9] in Japan have been made using tin flux for the growth. But process involving tin causes heavy doping and growth of high purity sample is very difficult by this method. Because of this reason we used co-crystallization at low temperature and high temperature grain growth methods.

In the case of co-crystallization method to grow β-Ga_2O_3 crystal, we used urea as nucleating agent. The gallium salt and urea were dissolved in the concentrate nitric acid. Since urea was a flux, we used urea and gallium oxide in 5:1 ratio. The temperature of the solution was raised to 50C in a small thermostat. After saturation of 24 hours, the temperature of the solution was decreased to crystallize the β-Ga_2O_3 crystal. The urea was removed by washing with water after crystal growth. The gallium oxide and urea or gallium oxide produced a green color partially dissolved material was observed. However, concentrated HNO_3 produced clear solution (Shown in **Figure 5**). There is traces of gallium chloride in presence of of HCl and excess HNO_3 was added to avoid chloride formation.

(a) (b)

Figure 5- (a) Green color partially dissolved gallium oxide nutrient (b) Transparent solution of Gallium oxide and urea in concentrate nitric acid that is suitable for crystallization and morphology of crystals obtained from this solution.

(a) (b)

Figure 6 - (a) Large number of small crystals nucleated together and (b) needle and prism crystals and bubbles were not observed.

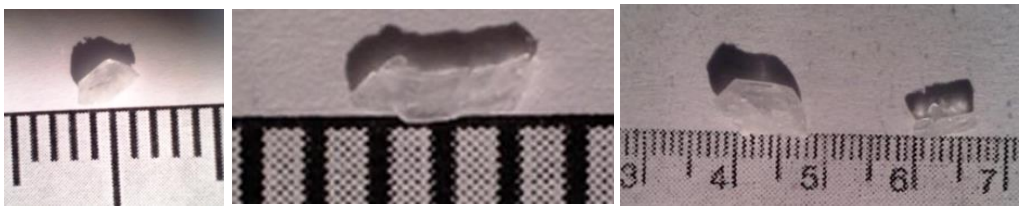


Figure 7- Prism and needle shaped crystals produced by co-crystallization method

Figure 7 shows as grown needles and prism type of β-Ga_2O_3 crystal. These needles in dilute concentration nutrient have very large aspect ratio. Experiments to optimize conditions to produce large crystals and alter morphology are continuing by this method. Crystals grown using urea at high temperature showed fat needles and prism morphology crystals. SEM morphology of these crystals is shown in Figure 3. We observed several small crystallites and step growth on the surface of large crystals. Gross defects such as voids, precipitates

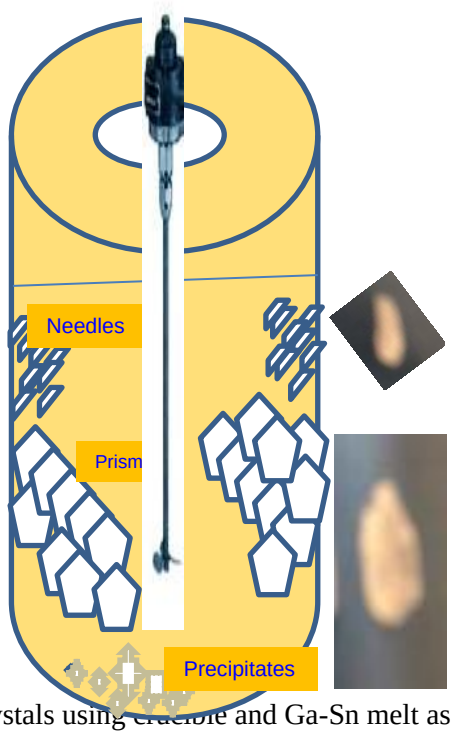
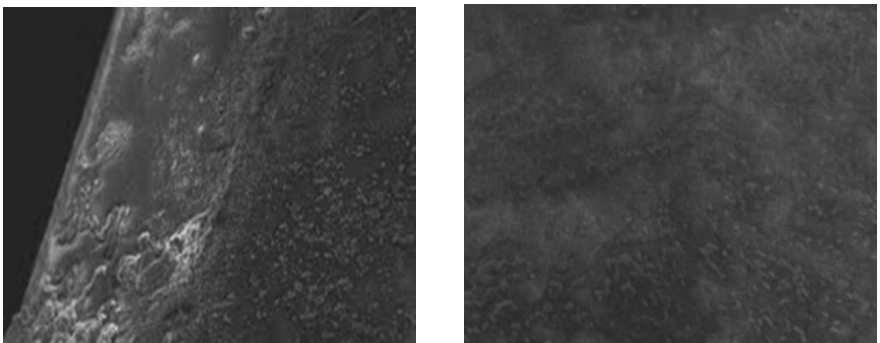


Figure 8- Growth of crystals using crucible and Ga-Sn melt as flux

In the second growth approach we placed the gallium salt in the alumina crucible with small amount of Ga-Tin mixture and raised the temperature slowly to 300 C. After soaking for a period 8-10 hours we raised the temperature to 1050 and left it for 25 hours. Small crystals grew on the surface of the crucible. These prismatic crystals were translucent. On the top portion of the flux, we observed needles. We observed precipitates in the bottom of the crucible. In this process it was difficult to control the morphology of crystals since we did not use prefabricated seeds. This result was similar to that reported in reference 6.

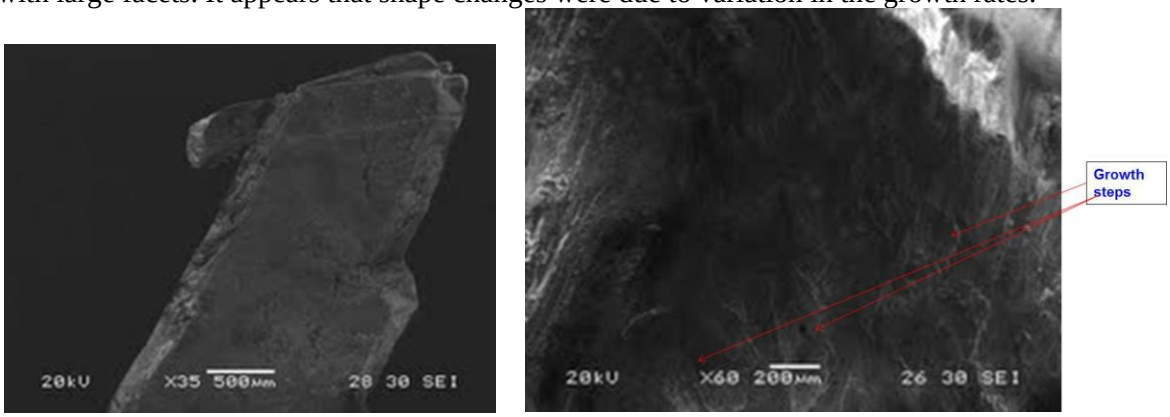
2.3 Fabrication and Characterization of crystals: As grown crystals cm size crystals were polished using water-glycol mixture. Crystals were characterized for the morphology by optical microscope and scanning electron microscope (SEM). The bandgap of the material was determined by studying the optical transparency and absorbance.



(a) (b)

Figure 9- SEM morphology of (a) Needle and (b) plate crystals. Needles showed large number of ridges on the surface.

A careful morphological examination of the morphology of the prism crystal showed growth steps (**Figure 10)** on the flat surfaces. Some of the steps were elongated as needles and some steps were flat with large facets. It appears that shape changes were due to variation in the growth rates.



(a) **(b)**

Figure 10- Growth steps shown on the surface of (a) needle and (b) prism (arrowed) crystals.

Preliminary X-ray diffraction data showed that lattice parameters a= 5.80A, b=305A and c=12.20A were in agreements with previously reported values. The bandgap of as grown crystal was measured by transmission and absorption data. We determined a value of 4.70eV a value slightly lower than predicted values of 4.9 eV. Further study in this area is continuing and we expect to achieve pure and better crystals for resistivity and bandgap measurements.

SUMMARY

We used low temperature flux method to grow 2H-SiC and (β–Ga_2O_3 crystals. SiC crystals nucleated as a disc in presence of AlN and then grew in the form of 2H-SiC thin film on the 6H-SiC substrate. Centimeter size single crystals of a novel bandgap material Gallium Oxide (β–Ga_2O_3) were grown by solution method. In the flux method we used tin and other metallic flux. This crystal was placed in an alumina crucible and temperature was raised above 1050 ºC. Crystals showed prismatic and needle shaped morphology. We observed faceted growth steps on the surfaces of large prism shape crystals. Bandgap measurement using the optical absorption curve indicated a bandgap of 4.7eV. Further study on purification and growth is continuing.

We used a flux and semi wet method to grow transparent good quality crystals. In the semi-wet method Ga_2O_3 was synthesized with starting gallium nitrate solution and urea as a nucleation agent.

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